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Metal−Organic-Framework-Type 1D-Channel Open Network of a Tetravalent Uranium Trimesate

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S *Supporting Information*

ABSTRACT: An uranium trimesate open framework is built up from trinuclear building blocks (μ_3-OU_3) connected to each other by tricarboxylate linkers to generate honeycomb-like 3D topology. This compound was solvothermally synthesized from low-valent uranium in an *N,N*-dimethylformamide solvent under an inert atmosphere, favoring stabilization of the tetravalent oxidation state, which is confirmed by X-ray photoelectron spectroscopy analysis.

For the past decade, the number of synthesis reports of metallic carboxylates has grown exponentially because of their implication in the construction of metal−organic frameworks (MOFs), exhibiting highly porous and fascinating atomic architectures.[1] Transition d or 4f block elements are the most used metals for the construction of such compounds, but actinide cations were also involved in the elaboration of a large variety of hybrid organic−inorganic assemblies. Since the use of the oxalate ligand in the industrial process for actinide extraction and separation, a significant effort has been focused on the reactivity of different organic polycarboxylate anions,[2] mainly with uranyl cations, UO_2^{2+}, either at room temperature or under mild hydrothermal conditions, resulting in multi-dimensional (1D, 2D, and 3D) extended uranyl−organic frameworks (UOFs).[3] Reduced oxidation states of uranium (V or IV) have been less investigated for this class of solids. Pentavalent uranium is known to rapidly undergo redox disproportionation to U^{IV} and U^{VI} cations in aqueous solution, and its isolation is very difficult in coordination complexes,[4] despite recent successes in the crystallization of large stable polynuclear species.[5] Although tetravalent uranium carboxylates have been identified for more than 50 years,[6] only a very few reports described the different varieties of its coordination complexes involved in low-dimensional networks.[7] In some cases, systems involving phthalic acid have been investigated in order to study polydentate interactions with U^{IV} in biological processes inducing redox reactions.[8]

Here we show that reactivity of the 1,3,5-benzenetricarboxylate (or trimesate, noted btc hereafter) linker with a source of uranium trichoride under solvothermal conditions gave rise to the formation of an unprecedented 3D framework, $U_3O(btc)_3(OH)(H_2O)_2\cdot 2.5DMF\cdot 1.5H_2O$ (**1**), involving μ_3-O trinuclear building blocks containing U^{IV}.

Green crystals (Figure S1 in the Supporting Information, SI) of **1** were prepared by using the solvothermal route under an inert atmosphere from the reaction of UCl_3 and trimesic acid in an anhydrous *N,N*-dimethylformamide (DMF) solvent at 150 °C for 24 h. Its single-crystal X-ray diffraction (XRD) analysis revealed an original extended open network with honeycomb-like topology. In a first approximation, uranium is 8-fold coordinated with six carboxyl O_c atoms, one terminal O atom, and one bridging O atom (Figure 1), defining a distorted trigonal-prismatic polyhedron. One of its square faces is capped by an O atom in the terminal position [U−O5 = 2.474(15) Å]. This bond length fits well with the existence of terminal H_2O species, in good agreement with the bond-valence-sum calculations (0.44).[9] The hypothetical presence of Cl^- anions (coming from the uranium source) is ruled out because the

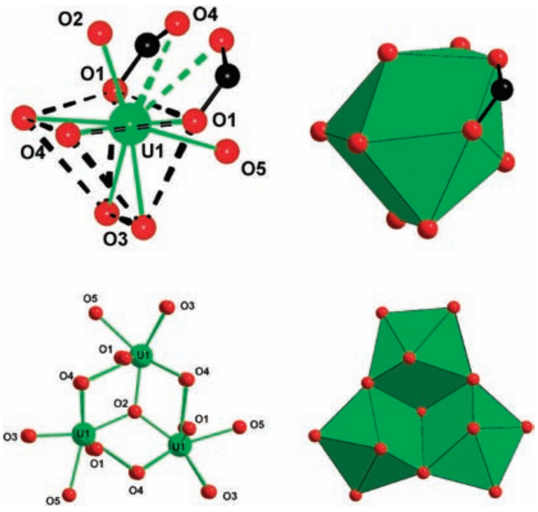

Figure 1. (top) Coordination environment around the center U1 in **1**. (U1−O1 = 2.465(11), Å, U1−O3 = 2.438(10) Å, U1−O4 = 2.419(10) Å. Dotted black lines indicate a trigonal prism with the two atoms O2 [μ_3-O; U1−O2 = 2.2254(7) Å] and O5 [terminal aquo group; U1−O5 = 2.474(15) Å] capping two of its square faces. The dotted green lines show two additional long U1−O4 bondings [2.918(10) Å]. (bottom) Trinuclear building motif with the specific μ_3-O group bridging the three U atoms.

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usual U−Cl distance is much longer (U−Cl > 2.6 Å).[10] Another oxo species (O2) also caps a second square face of the U-centered trigonal prism with a relatively short U−O2 distance of 2.2254(7) Å. It is shared between three U cations, in a strict trigonal plane (U1−O2−U1 angle of 120°), and this specific connection mode results in a μ_3-O-centered trinuclear core $U_3(\mu_3\text{-}O(O_c)_{18}(H_2O)_3$ (Figure 1).

A similar motif was previously mentioned in tetravalent uranium compounds,[10a,b,11] in which the bond lengths μ_3-O−U are in the range 2.20−2.28 Å. Each U-centered polyhedron is additionally linked to each other through two carboxylate arms of two distinct trimesate groups. One observes two long U1−O4 distances of 2.918(10) Å, which contribute to the coordination sphere around the U atom. In fact, the position of the U1 atom is slightly affected by these two neighboring carboxyl O atoms and shifted from the center of previously defined trigonal prisms toward the two additional O atoms with a deviation of ≈+0.4 Å. The trimeric units are then connected to each other through nine trimesate ligands. Two of the carboxylate arms adopt a syn−anti bidentate mode bridging two distinct U atoms. This induces the formation of rods developed along the *c* axis (Figure 2), with alternation of the trimers and part of three different organic ligands (1 and 3 positions of carboxylate groups). The latter connect two distinct trinuclear units to each other. The third carboxylate function (5 position) is bonded to one U atom belonging to a third trimer, in a symmetric chelating fashion, and ensures network tridimensionality in the *ab* plane.

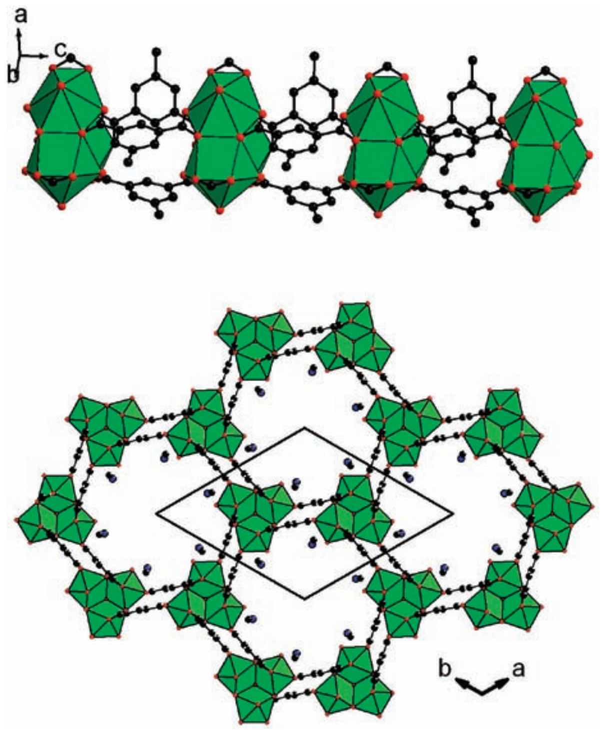

Figure 2. (top) View of rods from the connection mode of the trinuclear units with two of the carboxylate arms of the trimesate ligands along the *c* axis. (bottom) View of structure **1** perpendicular to the *c* axis, showing a honeycomb-like network of 1D channels of 11.2 Å. Fragments of DMF trapped within the channels are also indicated (blue/black circles).

The resulting framework (Figure 2) is reminiscent of a honeycomb-like net and delimits 1D channels extending along the *c* axis, with a free opening diameter of close to 11 Å (based on the ionic radius of 1.35 Å for oxygen) The tunnels are bound by the trimeric cores with terminal water species pointing toward their center and benzene planes of trimesates parallel to the channel axis. Interestingly, the atomic arrangement observed in **1** clearly shows that the driving force for crystal assembly is not given by the ternary symmetry of the trimesate ligand but rather by the symmetry of the inorganic building block itself. A similar structural feature was previously illustrated in the thorium trimesate TOF-2[12] or aluminum trimesate MIL-110.[13]

Only fragments of organic solvent are revealed from XRD analysis. DMF and H_2O molecules are assumed to fill the structure channels with a ratio of U_3/DMF/H_2O = 1/2.5/1.5 (from chemical and thermogravimetric analyses; Figure S4 in the SI). The presence of DMF is observed by ^{1}H NMR of the liquid resulting from the dissolution of phase **1** (Figure S3 in the SI). The occurrence of the oxygen ligand (oxo, hydroxo, or aquo) could be due to partial dehydration of the acid, which is known to lead to the production of anhydride and water. The latter reaction would be favored by the presence of Lewis acid (U^{III}) or Bronsted acid (HCl, from deprotonation of trimesic acid and chloride anions).

The chemical formula deduced from XRD analysis led to $U_3O(btc)_3(H_2O)_3$, with 11 negative charges for the network, which should be balanced by the charge from the three U cations. With a formal positive charge of 3.67 for a neutral framework, this should correspond to a mixed U^{III}/U^{IV} valence for uranium. The bond-valence-sum calculations from the parameters developed by Burns et al.[9] gave a value of 3.99 (or 4.37 with the two long U−O4 bonds), which is close to the formal valence 4+ for uranium. The tetravalent state was further confirmed by X-ray photoelectron spectroscopy (XPS) analysis. The U 4f XPS spectrum (Figures 3 and S6 in the SI) shows the binding energies located at 379.9 eV (fwhm =1.94) and 390.8 eV (fwhm =1.94) for the main U 4f$_{7/2}$ and U 4f$_{5/2}$ components, respectively. These binding energy values are comparable to those observed in U^{IV}-based compounds previously reported in the literature.[14]

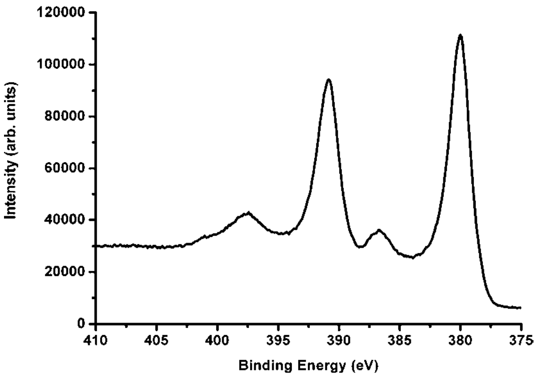

Figure 3. U 4f XPS spectrum of **1** (after 60 s of Ar$^+$ etching).

This analysis is consistent with the presence of U^{IV} only, and there is a need for additional negative charges for ensuring the electroneutrality of the structure. Cl^- anions could be present within the structure channels, but Castaing microprobe analysis indicated only a trace (U_3/Cl ≈ 24). Therefore, a partial OH/H_2O occupancy (with a OH/H_2O ratio of 1/2) is considered for the terminal U−O bonding. Such a statistical distribution was previously reported in other MOF compounds containing closely related μ_3-O trinuclear units.[15] It is noticeable that compound **1** is obtained from a trivalent uranium source. Oxidation into U^{IV} of the latter thus occurs during the hydrothermal treatment and could come from the presence of traces of O in the different starting reactants. This would give rise to the in situ conversion of U^{III} into U^{IV}, which favors the formation of the final structure (attempts using UCl_4 did not lead to the formation of the present phase). An oxidation of U^{III} in the presence of controlled amount of water was also described in literature and led to the crystallization of different U^{IV} and/or U^{V}-bearing complexes.[16]

The phase persists up to 240 °C under air and then transforms into α-U_3O_8 from 340 °C (Figures S4 and S5 in the SI). Moreover, slow oxidation is perceptible after long exposition (several days) in an air atmosphere. Attempts of Brunauer−Emmett−Teller surface area measurements were carried out from N_2 sorption with different degassing temperatures (100, 150, and 200 °C, under a primary vacuum), but no N_2 sorption capacity was observed. This result is quite unexpected regarding the potential porosity of the atomic structure, which would be compatible with N_2 diffusion within the tunnels. A similar behavior was previously reported in thorium trimesate (TOF-2[12]) with a closely related open framework. One explanation would be that the removal of encapsulated solvent molecules (DMF) is not efficient enough for the releasing porosity of this material.

This MOF phase opens the way to the construction of new extended architectures based on tetravalent uranium associated with carboxylate linkers. New crystal chemistry with low-valence-state uranium could thus be envisaged with O-donor ligands, also possibly offering novel opportunities toward the utilization of U-based compounds in catalysis.[17]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis procedures and analytical data, crystallographic data for **1** (CIF), SEM images, powder XRD patterns, IR spectrum, and detailed figures of the XPS spectrum (Figures S1−S7). This material is available free of charge via the Internet at http://pubs.acs.org. The file CCDC 832042 contains the supplementary crystallographic data. These data can also be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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■ DEDICATION

Dedicated to Prof. Gérard Férey on the occasion of his 70th birthday.

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